

Population pumping of vibrational and rotational quantum states in the triatomic hydrogen ion observed by electron-beam-assisted high-resolution spectroscopy

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We present a technique to observe the optical manipulation of individual quantum states of H_3^+ ions stored inside a heavy-ion storage ring, where the excitation is detected by electron-beam-assisted action spectroscopy. The transitions addressed here are chosen to enable multicolor spectroscopy of states far above the energetic barrier, where this molecule—with a triangular ground state—can sample linear geometries. This region of the spectrum has so far been inaccessible due to extremely weak direct transition strengths from the ground vibrational level. Our experiments pave the way for spectroscopy of the simplest polyatomic molecule in a previously unexplored energetic territory, which would benchmark theoretical data crucial for the understanding of this fundamental molecular system. Our results also demonstrate laser pumping to vibrationally and rotationally excited states of H_3^+ , gaining model-dependent access to their relative dissociative electron recombination rates.

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I. INTRODUCTION

Manipulation of individual quantum states of molecules by laser light is usually motivated by the aim of creating internally cold samples of molecules and the promise of superior control of chemical reactions [1,2]. In many cases, the formation of neutral molecules starts from samples of ultracold atoms, and the choice of the species is dictated by the preparation of the atomic precursors with a strong propensity for experiments involving alkali metals [3]. Most of the studied systems are diatomic molecules, where the number of rotational and vibrational states is still manageable, although, recently even polyatomic molecules have been cooled through optical transitions [4–7]. For efficient optical cycling, certain properties of the molecular systems, e.g., the existence of a strong electronic transition and favorable Franck-Condon factors have been emphasized [8].

Molecular ions have also been explored as candidates for optical pumping [9]. As ion trapping and sympathetic cooling are established techniques, the use of molecular ions can potentially broaden the applicability of the approach to species

that cover a larger fraction of the periodic table. This enabled experimental studies of light hydrides like AlH^+ [10], and a range of other diatomic ions were considered as candidates [11,12]. The full potential of optical cooling of molecular ions has been demonstrated in a remarkable series of experiments that succeeded to cool HD^+ ions to the rovibrational ground state [13] in order to obtain spectroscopic data of extremely high precision [14,15]. To the best of our knowledge, similar measurement schemes have not yet been applied to polyatomic molecular ions.

We present a very different optical pumping approach in which laser excitation and spontaneous decay are used to drive population out of one quantum state and accumulate it in others. We use optical transitions to manipulate the internal states of H_3^+ ions stored inside the nearly interaction-free vacuum of the Cryogenic Storage Ring (CSR) [16]. In our case, the goal is not to produce colder molecules, but to populate and study ions in specific vibrationally and rotationally *excited* states, and eventually to use these states as stepping stones for a new type of action spectroscopy. To this end, we separately depopulate the rotational ground states in the two nuclear spin configurations of H_3^+ using continuous-wave laser light. We thereby pump population into long-lived rovibrationally excited states and eventually reach stable population inversion for the lowest rotational states.

Since the triatomic hydrogen ion is the simplest polyatomic molecule, it is an important benchmark for quantum chemical calculations, and despite its structural simplicity, H_3^+ keeps challenging experimentalists and theorists alike. After the discovery of the molecule by J. J. Thomson in 1911 [17], it took nearly 70 years before the first laboratory spectrum

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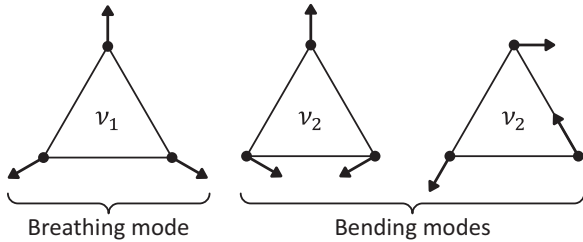
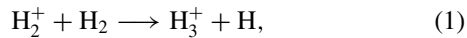


FIG. 1. Depiction of the vibrational normal modes ν_1 and ν_2 of the H_3^+ molecule.

was recorded by Oka in 1980 [18]. More than four decades of experimental efforts later, the highly excited states of H_3^+ remain elusive, leaving half of the energetic landscape up to the dissociation limit unexplored. Moreover, remarkably detailed predissociation spectra recorded close to the dissociation limit [19], containing more than 20 000 discrete lines [20], have yet to be assigned.

Apart from its fundamental relevance for the field of molecular physics, H_3^+ plays a central role in interstellar chemistry. Formed through cosmic-ray ionization of molecular hydrogen, followed by the very efficient ion-neutral reaction



triatomic hydrogen ions are among the most important molecules for the chemistry of the interstellar medium (ISM). As a strong proton donor, H_3^+ initiates a network of ion-neutral reactions that drive molecular synthesis in space, including the formation of water and organic molecules [21,22]. Since its abundance is directly linked with the cosmic-ray ionization rate and the ratio of molecular to atomic hydrogen, H_3^+ serves as a valuable diagnostic tool for diverse astrophysical environments [23].

In fact, very recently it has been suggested that the unexpected presence of very bright galaxies at high redshifts observed by the James Webb Space Telescope [24,25] may be explained by enhanced formation of hydrogen molecules through strong couplings between electronic states of the H_3^+ molecule [26]. This additional H_2 formation channel, at much higher redshifts than previously assumed, could have a massive impact on primordial chemistry. Thus, intrinsic properties of the excited-state surfaces of H_3^+ may be of great relevance to star formation in the early universe.

A. Spectroscopy of H_3^+

Structurally, H_3^+ is composed of three protons and two electrons, with two different nuclear spin configurations, *para* ($I = 1/2$) and *ortho* ($I = 3/2$), which interconvert only by proton exchange during chemical reactions [27]. In its ground state, it adopts the form of an equilateral triangle (Fig. 1). Owing to its symmetry, H_3^+ does not possess a permanent dipole moment, rendering pure rotational transitions dipole forbidden.

The absence of stable electronically excited states further restricts spectroscopy to rovibrational transitions. The vibrational modes of H_3^+ are shown in Fig. 1. Of the fully symmetric breathing mode ν_1 and the doubly degenerate bending

mode ν_2 , only the latter carries a small dipole moment and therefore qualifies as infrared active. The linear combination of the two bending modes can lead to angular momentum in the vibrational motion, which is denoted by the quantum number l . Vibrational states are typically labeled $\nu_1\nu_2^{|l|}$. Rotational states are characterized by the rotational angular momentum quantum number J (excluding spin) and its projection k onto the molecular axis, which is combined with the vibrational quantum number l into a new quantum number $G = |k - l|$ (see Lindsay and McCall [28] for nomenclature and quantum numbers). Spectroscopic investigations of H_3^+ rely on the ν_2 bending mode, its overtones, and ν_1 - ν_2 combination bands. Within the harmonic approximation, only transitions that change the vibrational quantum numbers ν_1, ν_2 by ± 1 are allowed. Therefore, transition strengths from the vibrational ground state to vibrationally excited states decrease sharply for higher-order transitions, inhibiting the spectroscopic accessibility of the excited states of this important species severely.

The first laboratory spectrum of H_3^+ was recorded in 1980 by Oka [18], employing a difference frequency laser system and a liquid-nitrogen-cooled multireflection discharge cell. Oka successfully recorded 15 lines in the infrared spectrum of the fundamental ν_2 band [18]. It took another 15 years, before Geballe and Oka detected three of these transitions in dense molecular clouds, marking the first observation of H_3^+ in the ISM [29] and confirming the prevalence of ion-neutral chemistry in interstellar space. Since then, H_3^+ has also been observed in diffuse clouds [30], planetary atmospheres [31,32], and even in extragalactic lines of sight [33]. These detections have played a crucial role in constraining the cosmic-ray spectrum [34]. A comprehensive review of H_3^+ astronomy is given by Miller *et al.* in Ref. [35].

The last 25 years have seen significant advances in the methods used for H_3^+ spectroscopy. In 2003, Gottfried *et al.* [36] reported the first measurements of transitions above the so-called barrier to linearity, at energies around $10\,000\text{ cm}^{-1}$ above the ground state, employing velocity and phase modulation in a discharge cell for enhanced sensitivity. Above this threshold, H_3^+ ions can access linear configurations [37], complicating theoretical treatment substantially. Observed transitions in this range are about 4 orders of magnitude weaker than those of the fundamental ν_2 band [38].

As traditional direct absorption spectroscopy reaches its sensitivity limits at these intensities, action spectroscopy has emerged as a powerful alternative. For this method, the absorption of a photon is transferred to a reaction, whose products can be detected with high sensitivity using mass-spectrometric particle detection techniques. Pioneered by Schlemmer and Gerlich for N_2^+ [39], the first chemical-probing action spectroscopy scheme of H_3^+ was demonstrated by Mikosch *et al.* in a cryogenic 22-pole ion trap, utilizing the endothermic reaction between buffer-gas cooled H_3^+ and Ar atoms [40]. Laser excitation of the third ν_2 overtone was successfully observed via the detection of ArH^+ ions, recorded with near-unity detection efficiency for individual H_3^+ ions.

Building on this technique, Kreckel *et al.* extended action spectroscopy to excited states above the barrier to linearity, obtaining results consistent with prior direct absorption spectroscopy experiments [41]. The energetically highest-lying

state that is both experimentally observed and fully assigned by theory was measured by Berg *et al.* [42,43] at an energy of $16\,700\text{ cm}^{-1}$, using the same technique. Notably, the target transition in this case was more than 6 orders of magnitude weaker than the fundamental ν_2 band. At the precision frontier, Jusko *et al.* used the combination of a 22-pole ion trap with a frequency comb to measure fundamental ν_2 band frequencies with an accuracy better than 1 MHz [44].

However, despite these advances in accuracy and sensitivity, more than half of the energetic landscape up to the dissociation limit at approximately $35\,270\text{ cm}^{-1}$ remains unexplored. Further progress is impeded by the increasingly weak transition strengths. On the other hand, even before many of these state-resolved spectroscopy efforts, Carrington *et al.* recorded a very detailed predissociation spectrum near the dissociation limit in 1982 [19]. Around $26\,000$ spectral lines were observed by photodissociation of highly excited H_3^+ ions in a molecular beam, using a CO_2 laser [20]. Despite numerous theoretical attempts [45–47], these spectra have remained unassigned for over 40 years. To close the energetic gap and shed light on the high-energy region, new spectroscopic techniques will have to be developed. The present work serves as an important step toward that goal.

B. Theoretical calculations

Most spectroscopic investigations have been closely guided by extensive theoretical efforts to compute the rovibrational level structure of H_3^+ . Pioneering work of Carney and Porter on the first *ab initio* potential energy surface (PES) and its associated vibrational spectrum [48,49] was instrumental in Oka's discovery of the fundamental ν_2 band [18].

To access higher vibrational excitations, Sutcliffe, Miller, and Tennyson developed a two-step variational approach for the calculation of rovibrational spectra of triatomic molecules [50–52]. Based on this method and the PES of Meyer *et al.* [53], Kao *et al.* published the first comprehensive H_3^+ linelist, comprising 699 transitions with level energies up to 8200 cm^{-1} [54].

However, the finite-basis-representation implementation used in this work is inadequate for states above the barrier to linearity, as its basis functions are not well suited for the linear geometries sampled in this region. To overcome this limitation, the discrete variable representation (DVR) developed by Bačić and Light was adopted [55]. This approach has proven to produce accurate results, enabling the creation of the seminal linelist by Neale *et al.* [56], based on the PES of Dinelli *et al.* [57]. The list includes over 3×10^6 transitions with level energies up to $15\,000\text{ cm}^{-1}$ and has been crucial for a vast number of astronomical and laboratory studies [36,38,41,43,58–61].

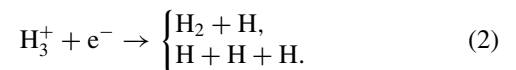
Building on the DVR framework and the PES of Pavanello *et al.* [62], Mizus *et al.* calculated an extended linelist containing more than 10^8 transitions with transition energies of up to $25\,000\text{ cm}^{-1}$, achieving an average standard deviation of 0.18 cm^{-1} [63] between theory and measurements over the range where experimental data are still available. Most recently, Bowesman *et al.* refined this linelist using empirical energy levels derived from a network of more than 1700 measured transitions [64].

While the low-energy spectrum is believed to be well understood, accurate predictions above the barrier to linearity remain challenging. Theoretical uncertainties exceed 1 cm^{-1} for levels above $20\,000\text{ cm}^{-1}$ [64], as predictions beyond $17\,000\text{ cm}^{-1}$ remain entirely unvalidated by experiment. Consequently, experimental measurements of highly excited states are essential for improving and validating theoretical models in this high-energy regime.

C. Dissociative electron recombination of H_3^+

In the present work, we will use the rate of neutral particles resulting from electron recombination of H_3^+ ions stored inside the CSR as a sensitive action spectroscopy signal. This method requires a change in the recombination rate for the excited states of H_3^+ compared to the ground state.

In general, the recombination of small molecular cations with free electrons leads to the dissociation of the neutral product molecules, as the recombination energy typically exceeds the molecular binding energy. Consequently, for H_3^+ , the capture of a free electron will result in dissociative recombination (DR) according to



The DR reaction of H_3^+ is one of the key processes for the chemistry of the cold diffuse ISM, where low temperatures and densities prevail. As the lowest rotational states dominate in the ISM, a lot of effort went into the determination of the DR rate coefficients of internally cold H_3^+ [34,65–67] and its isotopologues [68,69].

With the recent surge in modeling of (exo)planetary atmospheres at elevated temperatures, the DR of excited molecular ions has come into focus, but experimental data on the DR of excited states are extremely sparse. While there are a few dedicated measurements of the DR rates of vibrationally excited diatomic ions, like H_2^+ [70], He_2^+ [71], and O_2^+ [72], only rather unspecific experimental information on the electron recombination for excited states of polyatomic ions is available. For example, Hus *et al.* [73] observed slower electron recombination rates for H_3^+ ions in single pass merged-beam studies using ion source settings that were meant to favor the collisional cooling of vibrational states prior to the recombination measurements.

Theoretical treatments of the DR process for polyatomic ions also present a formidable task, and the H_3^+ ion has received a lot of attention [74]. Initial studies suggested a very low recombination rate. However, this notion was corrected when the Jahn-Teller effect was identified as the driver of the recombination process at low energies [75,76]. Today, state-of-the-art calculations agree fairly well on the absolute scale of the H_3^+ DR rate coefficient [77,78] and predict a significant increase in the DR rate for vibrationally excited states [77]. In the present study, this enhancement in the DR rate following laser excitation is used as a diagnostic signal for high-resolution spectroscopy. Combined with a comprehensive excitation model, our measurements provide the first conclusive experimental information on the DR rate coefficient of the H_3^+ ion in specific excited states.

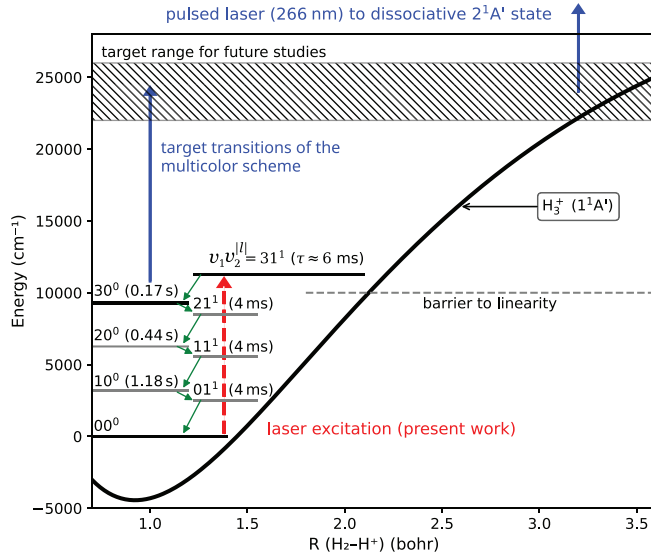


FIG. 2. Overview of the energetic landscape of H_3^+ . The thick black line depicts a cut through the ground-state potential energy surface in Jacobi coordinates. The red dashed arrow marks the laser excitation step used in the present work, while the green arrows depict the vibrational cooling after excitation. As the full cooling cascade actually comprises many rovibrational states with individual lifetimes, we give only coarse values for the lower vibrational levels here, corresponding to the “rotationless” calculations of the spontaneous decay for the vibrational band origins given by Dinelli *et al.* [79]. The blue arrows depict the additional steps proposed for the multicolor spectroscopy scheme of Znotins *et al.* [80]. The target energy range for the full scheme is marked by the hatched region. From this energy region, efficient direct single-photon UV photodissociation is possible with conventional pulsed laser systems.

II. SIMULATION OF POPULATION DYNAMICS

To extend the reach of H_3^+ laser spectroscopy to energies above $20\,000\text{ cm}^{-1}$, Znotins *et al.* proposed a multicolor action spectroscopy scheme [80]. An overview of the H_3^+ energetic landscape with features relevant for the present work is given in Fig. 2. The multicolor approach relies on a two-step excitation process, starting from individual rotational states in the vibrational ground state. In the first step, a laser transition to a state above the barrier to linearity is initiated, where the excited state is carefully chosen such that the population will decay spontaneously into an intermediate metastable state with high probability. The metastable state features multiple quanta in the vibrational v_1 breathing mode, which gives it a comparatively long lifetime of more than 100 ms [80]. From that metastable state, a second laser transition leads into the target energy range from $22\,000$ to $26\,000\text{ cm}^{-1}$. From this energy region, direct single-photon UV photodissociation is possible with conventional pulsed laser systems [81], enabling very efficient coincidence detection of the dissociation products for experiments with molecular beams.

The strategy outlined above avoids direct one-photon excitation from the vibrational ground state, as the transitions leading to states above $20\,000\text{ cm}^{-1}$ are at least 9 orders of magnitude weaker than the fundamental band. To find optimized excitation pathways, Znotins *et al.* developed a

comprehensive master equation model to predict the time-dependent state populations arising from the interaction of stored H_3^+ ions with laser radiation. The full model included around 40 million transitions, and it is based on a set of coupled ordinary differential equations that describe the transfer between individual state populations P_i in an external radiation field with spectral energy density $\rho(\nu)$. The transition probabilities are included according to the Einstein coefficients for spontaneous emission A_{21} and absorption B_{12} . The master equation can be summed up as

$$\begin{aligned} \frac{dP_i(t)}{dt} = & -\sum_j A_{ij}P_i(t) - \sum_k B_{ik}\rho(\nu_{ik})P_i(t) \\ & + \sum_k A_{ki}P_k(t) + \sum_j B_{ji}\rho(\nu_{ji})P_j(t), \end{aligned} \quad (3)$$

where the index i runs over all states in the model, while the indices j and k account for all states energetically below and above state i , respectively. The Einstein coefficients were adopted from the ExoMol linelist described by Mizus *et al.* [63]. We will use a reduced version of this model (based on the updated linelist of Bowesman *et al.* [64]) to simulate time-dependent populations of all states following the first laser excitation step of the spectroscopy scheme, as indicated by the red and green arrows in Fig. 2. For a more in-depth discussion of the full multicolor scheme, the reader is referred to the original publication [80].

In the present work, we will demonstrate the successful implementation of the first excitation step by means of an electron-beam-assisted spectroscopy scheme with H_3^+ ions stored inside the CSR. We will focus on two transitions to states above the barrier to linearity; one transition with the rotational ground state in the para nuclear spin configuration as initial state, and one with the ortho ground state as initial state. Both transitions are viable candidates for achieving a substantial increase of population in the metastable $v_1v_2^{|l|} = 30^0$ vibrational state, such as to base the multicolor scheme on the accumulated population in this metastable level. The energies, quantum numbers, and lifetimes of the relevant states are given in Table I. For this pumping step, a continuous-wave laser is used. The spectral energy density ρ_L of the laser beam depends on the laser power P_L , the root-mean-square (rms) laser linewidth $\Delta\nu_L$, and the beam radius r_L . We use the spectral density for a collimated, homogeneous cylindrical beam with a Gaussian spectral profile around the central frequency ν_c , given by

$$\rho_L(\nu) = \frac{P_L}{\pi r_L^2 c} \times \frac{1}{\sqrt{2\pi} \Delta\nu_L} \exp\left(-\frac{(\nu - \nu_c)^2}{2\Delta\nu_L^2}\right). \quad (4)$$

Aside of the laser power and linewidth, the efficiency of the population transfer will also depend on the effective Doppler width, induced by the momentum spread of the ion beam inside the CSR, and on the overlap between the ions and the laser beam. As a starting point, we adopt the following parameters, slightly modified from the original model [80]: We assume an rms ion beam momentum spread of

TABLE I. State energies and quantum numbers for the two transitions addressed in the present work. The nuclear spin I , the state energy $\tilde{E} = E/hc$ (in cm^{-1}), the radiative spontaneous decay lifetime τ (in ms) for the excited states, and the relevant vibrational and rotational quantum numbers are given. All parameters are listed as reported by Bowesman *et al.* [64]. The state energies are given relative to the Pauli-forbidden $00^0(0, 0)$ nominal ground state of H_3^+ , which is commonly used to define the origin of the energy scale.

I	Initial state		Transition state			Metastable state		
	$\tilde{E}$	$v_1 v_2^{[I]}(J, G)$	$\tilde{E}$	τ	$v_1 v_2^{[I]}(J, G)$	$\tilde{E}$	τ	$v_1 v_2^{[I]}(J, G)$
1/2 (para)	64.12	$00^0(1, 1)$	11 323.10	5.9	$31^1(0, 1)$	9311.38	166	$30^0(1, 1)$
3/2 (ortho)	86.96	$00^0(1, 0)$	11 405.04	5.8	$31^1(1, 0)$	9333.13	167	$30^0(1, 0)$

$\Delta p/p = 2.3 \times 10^{-4}$ and a collinear overlap length of 4.26 m for ideally merged homogeneous ion and laser beams with 2 mm diameter each. The large discrepancy between the laser linewidth $\Delta \nu_L$ (on the order of 1 MHz) and the Doppler broadening of the ion beam (estimated to be ~ 500 MHz rms width) is taken into account by integrating the product of the laser spectral linewidth and the distribution function of the Doppler profile imposed by the ion beam velocity spread across all frequencies, yielding an effective spectral density experienced by the ions. This approach is based on the expectation that, over successive revolutions in the ring, elastic electron-ion interactions in the electron cooler (discussed in Sec. III) will in a steady state completely mix the velocities of individual ions within the momentum spread of the stored ion ensemble. We assume that 30% of the H_3^+ ions initially occupy the para rotational ground state $00^0(1, 1)$ and 25% occupy the ortho rotational ground state $00^0(1, 0)$. This ratio is based on an independent evaluation of the internal excitation within the ion source [82] that we used for the present experiment. More details on the experimental setup and conditions will be given in the next section.

The simulation results are presented in Fig. 3. The metastable state populations shown in Fig. 3(a) reach a maximum of 3.5% and 6% for the transitions from the para and ortho ground states, respectively, and decay rapidly as the respective ground states are depleted by the laser. However, considering the total population of vibrationally excited states, including the lower levels reached during the decay cascade shown in Fig. 3(b), maxima of $\sim 15\%$ are reached. This fraction decays much more slowly due to the longer lifetimes of the lower levels in the cascade, with around 7% of the ions remaining vibrationally excited even after 4 s. For the present detection scheme, the signal is expected to arise not solely from the metastable 30^0 state, but from any excited state with an increased DR rate coefficient after laser excitation as predicted by theory for the first vibrationally excited states of H_3^+ [77]. Therefore, the population fractions summed over all vibrationally excited states, shown in Fig. 3(b), are probably more relevant for the present study, while the excitation in only the 30^0 metastable state, shown in Fig. 3(a), will become relevant for future implementations of the full multicolor spectroscopy scheme.

Figures 3(c) and 3(d) show the simulated populations of individual states for the targeted para and ortho transitions, respectively. The depletion of the para and ortho rovibrational ground states is clearly visible. Although the population in the 30^0 metastable state diminishes quickly, other long-lived excited states at lower energies are subsequently populated,

surpassing the population in the metastable state after roughly 0.5 s. While the population of the vibrationally excited states begins to decline within the first 2 s of laser excitation, very long-lived, purely rotationally excited states of the para and ortho vibrational ground levels effectively trap the population and ultimately dominate.

III. EXPERIMENTAL SETUP AND MEASUREMENT SCHEME

A. Cryogenic storage ring, ion production, and injection

The experiments were carried out at the CSR facility [16] of the Max-Planck-Institut für Kernphysik in Heidelberg, Germany (Fig. 4). The CSR is a fully electrostatic cryogenic heavy-ion storage ring with a circumference of 35 m, designed to store beams of anions and cations with energies of up to 300 keV per unit charge. The inner vacuum chamber can be cooled by a closed-cycle liquid helium system to temperatures around 5 K, at which most residual gases are cryopumped efficiently. The subsequent low residual gas density on the order of 10^3 – 10^4 particles/ cm^3 allows very long storage times in an essentially collision-free environment, facilitating the accumulation of metastable excited-state populations in our experiment. A detailed review of the CSR is presented in Ref. [16].

For the present experimental scheme, a significant population fraction in the para and ortho rotational ground states of the ions is crucial. However, the production of H_3^+ in standard ion sources, proceeding through the exothermic reaction of Eq. (1), is known to result in highly excited ions [83]. While vibrational excitations of H_3^+ decay within the first 2 s of storage [59], rotational excitations can persist for several months in a collision-free environment owing to the lack of a permanent dipole moment [84]. Therefore, an active cooling mechanism is required to produce H_3^+ in its lowest rotational states prior to injection into the CSR. To this end, a pulsed supersonic gas expansion ion source was developed, capable of generating intense bursts of H_3^+ ions with minimal shot-to-shot fluctuation [82]. Prior to the experiment, the internal energy of the produced H_3^+ ions was characterized at the Université catholique de Louvain in Louvain-la-Neuve, Belgium. The measurements were based on the observation of the three-body kinetic energy release from the dissociative charge exchange between H_3^+ ions and an effusive jet of alkali metal atoms. These experiments revealed that around 55% of the H_3^+ ions in the pulse occupy either the para (30%) or the ortho (25%) rotational ground state [82].

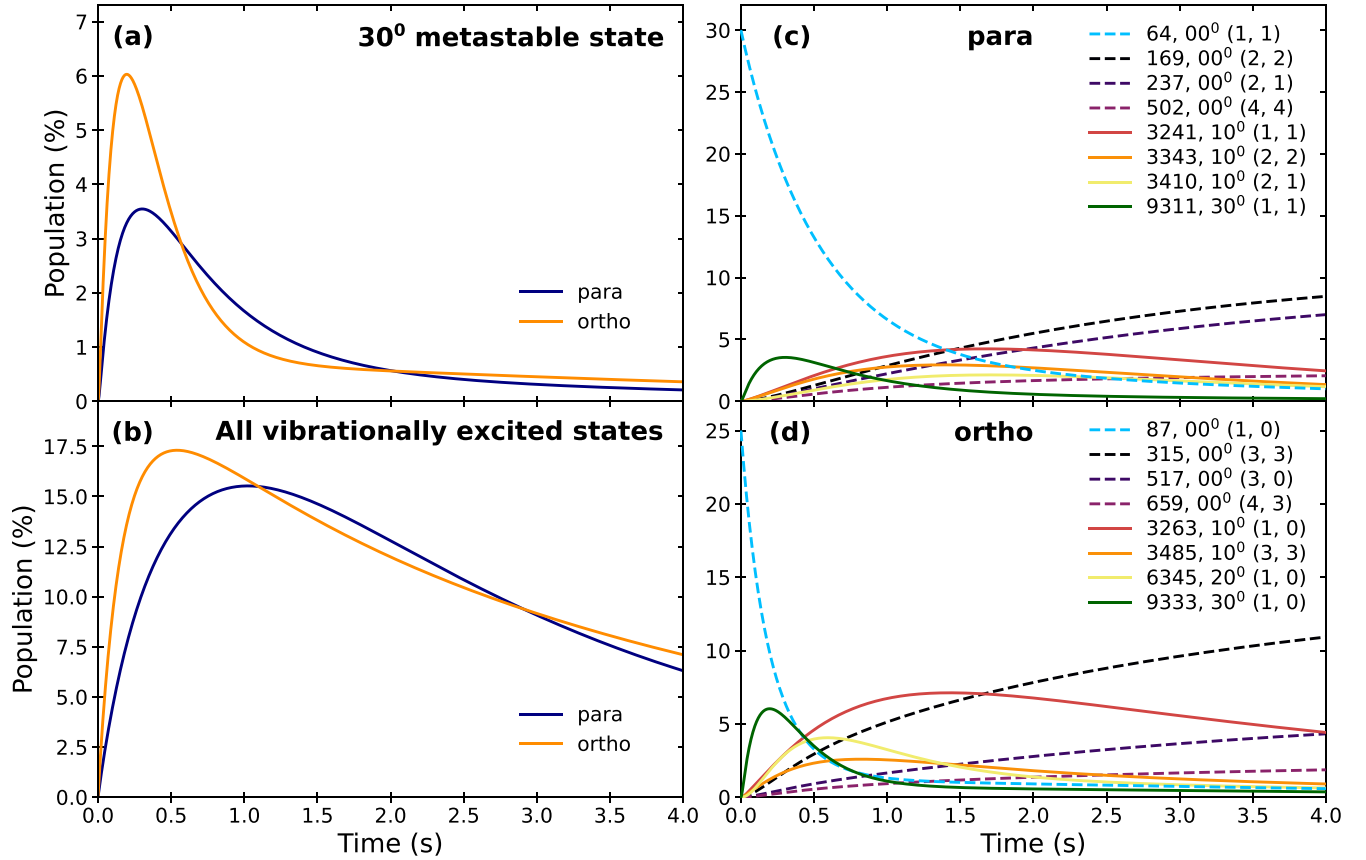


FIG. 3. Simulated relative state populations of H_3^+ ions in a continuously acting laser field driving the para and ortho transitions specified in Table I, respectively, within the independent manifolds of the two nuclear spin symmetries. The laser parameters including the geometrical overlap and the initial level populations are chosen for the CSR experimental conditions (see the text). (a) Population of the metastable vibrational 30^0 state as a function of time for the para and ortho transitions, as indicated. (b) Populations summed over all vibrationally excited states of a given nuclear spin symmetry as a function of time. (c)/(d) Evolution of individual populations of the most relevant states of para/ortho symmetry, using full lines for vibrational and dashed lines for rotational excitation together with the para/ortho ground states (light blue); inset labels in these panels indicate the energy $\tilde{E}$ (in cm^{-1} , rounded) of the states relative to the nominal ground state, and the vibrational and rotational quantum numbers $v_1 v_2^{||l}$ (J, G).

B. Electron cooler and particle detector for recombination measurements

1. Electron cooler setup

The storage ring is equipped with an electron-ion merged-beam setup, a so-called electron cooler, which serves a dual purpose: phase-space cooling of the stored ion beam [85] and enabling electron-ion recombination studies. The latter capability is particularly important for the measurements described here, as the recombination signal provides a sensitive probe to detect changes in the state distribution of the stored ions. Recent electron recombination measurements at the CSR have been described in detail in Refs. [86–89].

Located in one of the straight sections of the CSR (see Fig. 4), the electron cooler provides a velocity-matched, magnetically confined, nearly monoenergetic electron beam with a thermal energy spread of ~ 2 meV that is merged collinearly with the ion beam over a ~ 0.8 m long region.

2. Relevance of electron-ion collisions for the spectroscopy scheme

Coulomb collisions between the ions and the cold electrons reduce the ion beam momentum spread and the diameter of

the stored beam significantly [85]. The resulting momentum spread corresponds to a Doppler broadening of the ion beam of ~ 500 MHz rms width, which exceeds the laser linewidth of ~ 1 MHz rms width.

Because the ion beam's Doppler width far exceeds the laser linewidth, only a small fraction of the ions are in resonance with the laser at any given time. However, the frequent Coulomb collisions inside the electron cooler lead to a diffusion process that mixes the ions' relative velocities, ensuring that on consecutive revolutions all ions are addressed by the laser beam and “hole burning” is avoided; i.e., the laser does not simply deplete the narrow velocity subgroup of ions initially in resonance, thereby ending the laser-ion interaction, but continues to pump newly remixed ions into excited states over time. This continuous velocity remixing is therefore essential for achieving efficient optical pumping of the full stored ion ensemble over the course of a measurement.

3. Neutral particle detection

Variations of the neutralized particle count rate resulting from recombination of H_3^+ ions inside the electron cooler

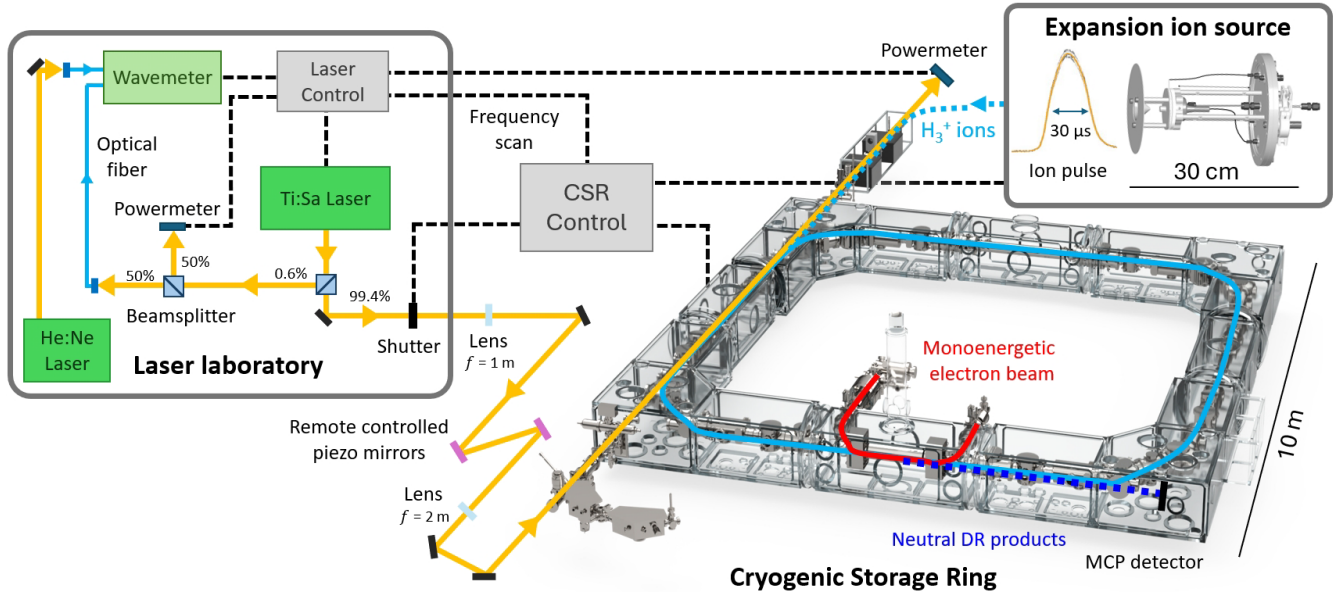


FIG. 4. Overview of the CSR with the experimental setup. The laser-ion interaction region extends along the straight injection section of the storage ring. The electron beam and the MCP detector, recording the neutral DR products, are marked. Schematics of the laser laboratory and the supersonic gas expansion ion source are depicted in the insets.

serve as a sensitive signal for our action spectroscopy scheme. The neutral H_2 and H fragments produced in the recombination process [Eq. (2)] are detected by a large microchannel plate (MCP) based detector downstream of the electron cooler (Fig. 4), with a dark count rate of $\sim 55 \text{ s}^{-1}$ and a detection efficiency of ~ 0.6 .

C. Laser

The laser system consists of a continuous-wave Sirah Matisse Ti:Sapphire (TiSa) ring laser, pumped at 532 nm by a 25 W Spectra-Physics Millennia laser. This configuration yields up to 5 W of output power with a spectral bandwidth of 1 MHz. The frequency is monitored using a HighFinesse WS7 wavemeter, calibrated against a frequency-stabilized He-Ne laser. Frequency stabilization of the TiSa laser is maintained via a proportional-integral-derivative (PID) feedback loop, which adjusts a piezoactuated cavity mirror based on the wavemeter readout.

The laser beam is guided from an enclosed laser area to the CSR via a dedicated beam transfer line, entering and exiting the experimental vacuum through borosilicate windows with a transmission of 93% at the target frequencies. A triggerable shutter placed before the transfer line enables rapid beam blocking. Within one of the straight sections of the CSR, the laser beam is overlapped collinearly with the stored ion beam to maximize the geometric overlap, creating an interaction region of 4.26 m. Alignment is achieved over a free-flying distance of 35 m using a set of 4.5 mm diameter apertures behind the interaction region, which were prealigned with a telescope during the construction of the CSR. Two piezoactuated mirrors permit precise beam steering during the alignment process. The transmission through the CSR during the measurements was 73%, resulting in a stable effective laser power of 4 W in the interaction region. Lenses in the transfer line

focus the laser beam to a diameter of 2 mm at the center of the interaction region, as determined by standard ray transfer (ABCD matrix) calculations, which propagate the Gaussian beam parameters through the sequence of lenses and free flight distances in the transfer line [90]. Although direct access to the beam within the interaction region is not possible, beam profile measurements before and after this region agree well with the matrix calculations.

D. Measurement scheme

Typically, several 10^6 H_3^+ ions from the pulsed supersonic gas expansion source (described in Sec. III A) were injected into the CSR at an energy of 59.7 keV. The velocity-matched electron beam, with an energy of 10.92 eV, a diameter of 12.5 mm, and a near-homogeneous density of $\sim 1 \times 10^5 \text{ cm}^{-3}$ ($3.7 \mu\text{A}$ current), was guided by an axial magnetic field of 6 mT.

During each injection cycle, the ions were first continuously electron cooled for 3 s, while the laser shutter remained closed. This initial precooling phase reduced the transverse size and momentum spread of the ion beam and established reproducible initial conditions for the spectroscopy phase. Throughout the precooling phase, the rate of neutral particles $R_{\text{e-on}}^{\text{pre}}$ at the MCP detector was continuously recorded.

Then, the laser shutter was opened for 4 s to probe the laser-ion interaction at a fixed frequency ν . The duration was adapted to the time span over which simulations (Sec. II) predict the most significant changes in internal level populations. During laser exposure, the electron cooler was periodically switched between 80 ms of electron cooling and 10 ms without electrons, with a 5 ms pause after each step to let the voltage output of the switching power supply stabilize. The typical count rate of neutral products at the MCP detector was around 6000 s^{-1} during electron cooling. Without

electrons, the neutral count rate dropped to $\sim 1000 \text{ s}^{-1}$, with the remaining signal dominated by neutralization of H_3^+ by residual gas interactions.

Gated neutral rates $R_{\text{e-on}}$ and $R_{\text{e-off}}$ were thus recorded with and without electrons, respectively. We verified that the laser exposure, even on resonance, does not affect the neutral rate arising from residual gas interactions, ensuring that $R_{\text{e-off}}$ is independent of the laser frequency. Consequently, the difference $R_{\text{e-on}}(\nu) - R_{\text{e-off}}$ is interpreted as the DR rate under laser exposure, $R^{\text{DR}}(\nu)$, which provides the laser frequency-dependent signal for the action spectroscopy scheme. Moreover, the average ion beam lifetime during continuous electron cooling was found to be approximately 430 s, governed by ion loss through the steady DR rate, implying that the total ion number decreases by less than 1% during the 4-s-long laser exposure period. Under these conditions, the measured spectroscopic signal in good approximation reflects the laser-induced variation of the sample-averaged DR cross section.

After this measurement period, the electron beam was turned off and the laser blocked for 1 s, before the remaining ions were dumped. In the time gap preceding the next injection the PID-stabilized laser frequency was adjusted to the next scan step, allowing sufficient time for frequency stabilization before the shutter was opened in the course of the next injection cycle. Including data acquisition, a full injection cycle lasted ~ 12 s. A scan consisted of one injection for each of the 51 laser frequencies, covering a range of approximately 3 GHz ($\sim 0.1 \text{ cm}^{-1}$) at a step size of 60 MHz ($\sim 0.002 \text{ cm}^{-1}$).

Each measurement run comprised several repeated scans across the full frequency range, performed with alternating scan direction to check for systematic drifts or slow variations in beam alignment. The central frequency and amplitude obtained from independent scans agreed to within their statistical uncertainties, with no systematic dependence on scan direction observed. No significant drift was observed over the several-hour duration of a measurement run, supporting the assumption of stable experimental conditions underlying the analysis outlined in the next sections.

IV. RESULTS

A. Spectroscopic signal

Monitoring the DR rate $R^{\text{DR}}(\nu)$ enables us to detect changes of the excited-state population within the stored ion ensemble to the extent at which the DR cross section of H_3^+ depends on the internal excitation of the ion. For this, we consider the DR rate under laser exposure, $R^{\text{DR}}(\nu)$, relative to the DR rate R_0^{DR} for the initial ion ensemble, under the assumption that the total number of ions is constant. Weighted by the laser-induced changes in internal-state populations, the ratio $R^{\text{DR}}(\nu)/R_0^{\text{DR}}$ reflects the relative state-dependent changes of the DR cross section.

The reference rate R_0^{DR} is measured during the precooling phase of the *same* injection cycle, before the laser shutter opens, and therefore reflects the DR rate of the unperturbed initial ion ensemble for that specific injection. Normalizing to this per-injection reference—rather than to a fixed calibration value or an average over injections—ensures that shot-to-shot

fluctuations in the number of stored ions cancel out in the ratio $S_{\text{DR}}(\nu)$, since both $R^{\text{DR}}(\nu)$ and R_0^{DR} scale with the same ion number.

For a measurement run as described in Sec. III D, the reference DR rate R_0^{DR} is obtained from the neutral count rate observed during the precooling phase, $R_{\text{e-on}}^{\text{pre}}$. The ratio

$$S_{\text{DR}}(\nu) = \frac{R^{\text{DR}}(\nu)}{R_0^{\text{DR}}} = \frac{R_{\text{e-on}}(\nu) - R_{\text{e-off}}}{R_{\text{e-on}}^{\text{pre}} - R_{\text{e-off}}} \quad (5)$$

is determined for each injection cycle, thus suppressing the effect of fluctuations in the number of stored ions between these cycles. To focus on the dependence on laser frequency, all results $S_{\text{DR}}(\nu)$ obtained at the same frequency ν are averaged. Moreover, in the reference DR rate R_0^{DR} , the use of the terms $R_{\text{e-on}}^{\text{pre}}$ and $R_{\text{e-off}}$ can be justified—although they stem from different time windows after injection—since the time differences are very small compared to the ion beam lifetime.

Measurement runs were performed with two laser scan ranges around the Doppler-shifted transition frequencies listed in Table I for the para and ortho spin symmetries, respectively. In both runs, the signal $S_{\text{DR}}(\nu)$ increased by $\sim 4\%$ near the respective target frequencies in distinctive spectral peaks. This is in qualitative agreement with theoretical predictions [77] and with the experimental findings of Hus *et al.* [73], if we assume successful optical pumping of a significant population fraction into vibrationally excited states. The widths correspond to the expected Doppler broadening of the laser frequency in the ion rest frame.

We fit the signal $S_{\text{DR}}(\tilde{\nu})$, expressed by the wave number $\tilde{\nu}$ of the laser, by a Gaussian

$$g(\tilde{\nu}) = c_0 + A_{\text{R}} e^{-(\tilde{\nu}-\mu)^2/2\sigma^2}, \quad (6)$$

with central frequency μ , width σ , amplitude A_{R} of the laser-induced resonance signal, and an offset c_0 . The offset is found to be $c_0 = 1.040(1)$ for the para and $c_0 = 1.057(2)$ for the ortho transition. For the present measurement scheme, the deviations of these offsets from unity reflect the slightly smaller number of ions expected to be in spatial overlap with the electron beam during the electron precooling phase, in which the rate $R_{\text{e-on}}^{\text{pre}}$ used to determine the reference DR rate R_0^{DR} was measured. The resonance signals $S_{\text{R}}(\tilde{\nu}) = S_{\text{DR}}(\tilde{\nu}) - c_0$ (subtracting c_0 as fitted for the respective run) are shown in Fig. 5.

The choice of a Gaussian line shape is motivated by the underlying broadening mechanism: The observed linewidth is dominated by the Doppler broadening of the ion beam's velocity distribution, which is expected to approach a Gaussian velocity profile. Other contributions to the line shape are negligible in comparison: The natural linewidth of the excited states, given their radiative lifetimes of ~ 6 ms (Table I), is of order 10 – 10^2 Hz, and the laser linewidth (~ 1 MHz) is more than 2 orders of magnitude smaller than the observed resonance width. Given the extreme weakness of the target transitions, power broadening is expected to be negligible as well. A Voigt profile was therefore not considered necessary, as any Lorentzian contribution would be several orders of magnitude narrower than the Doppler width and would not be resolvable at the present statistical precision. The residuals

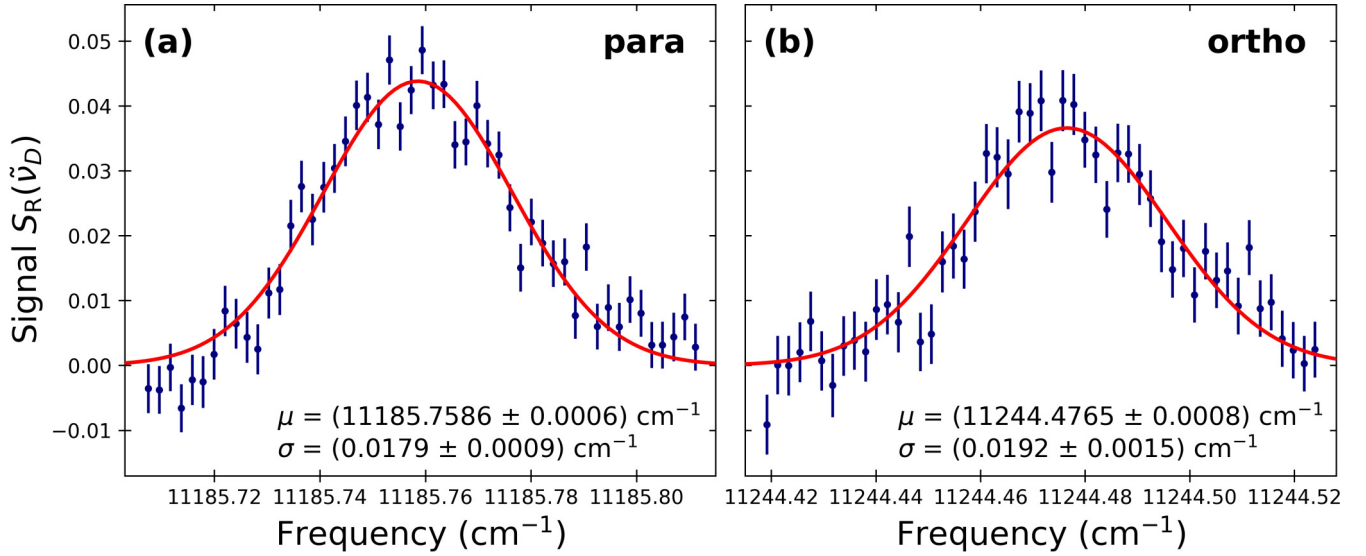


FIG. 5. Resonant electron-induced neutral signal $S_R(\tilde{\nu}) = S_{DR}(\tilde{\nu}) - c_0$ as a function of the laboratory-frame laser frequency for both transitions from (a) the para and (b) the ortho ground states as measured in the laboratory frame of the laser system. The signals (blue markers) are fitted by Gaussians (red lines) with given mean μ and standard deviation σ .

of the Gaussian fits do not show systematic deviations beyond statistical scatter.

The central frequencies yield the observed transition wave numbers $\tilde{\nu}_D = \mu$ listed in Table II, which refer to the laboratory frame and are, hence, Doppler shifted with respect to the ion rest frame. Applying the Doppler correction factor of 1.006 534(9), with its systematic uncertainty discussed below, the deduced transition wavenumbers $\tilde{\nu}_0$ in the ion rest frame are in reasonable agreement with the literature values of the target transition frequencies (see Table II). Moreover, the difference of $59.102(19) \text{ cm}^{-1}$ between the experimental values of $\tilde{\nu}_0$ measured for the para and ortho transitions is practically unaffected by the uncertainty of the Doppler correction factor and agrees perfectly with the difference of $59.109(14) \text{ cm}^{-1}$ between the literature transition frequencies. Based on this result, we demonstrate successful implementation of the first excitation step of the multicolor action spectroscopy scheme for both target transitions from the para and ortho rotational ground states, respectively.

Although the Gaussian fits yield a statistical uncertainty of just $7 \times 10^{-4} \text{ cm}^{-1}$ for the central transition frequency (corresponding to $\sim 20 \text{ MHz}$), the absolute accuracy is dominated by systematic uncertainties. The specified accuracy of the wavemeter is $2 \times 10^{-3} \text{ cm}^{-1}$, further limited to $5 \times 10^{-3} \text{ cm}^{-1}$ by the multimode fiber that was used to couple the laser into the device. In addition, the wavemeter was calibrated against a He-Ne laser with a frequency known to an accuracy of $1.2 \times 10^{-2} \text{ cm}^{-1}$. Combined, these factors contribute to the total systematic uncertainty of $1.3 \times 10^{-2} \text{ cm}^{-1}$ for the transition frequencies $\tilde{\nu}_D$ in the laboratory frame listed in Table II. While this systematic uncertainty is significantly larger than the statistical uncertainty for the central frequency of the fits, it could be improved by straightforward upgrades to the optical setup.

To determine the transition frequency in the rest frame of the H_3^+ ions, the ion velocity must be precisely known. At the CSR, the velocity is derived from the revolution frequency of the ions in the ring, measured to high precision by a

TABLE II. Measured transition frequencies $\tilde{\nu} = \omega/2\pi c$ (given in cm^{-1}) from this work, alongside their assignments, previous measurements, and theoretical predictions. The first column gives the nuclear spin quantum number I . Frequencies from the present measurements are given in both the laboratory frame ($\tilde{\nu}_D$, Doppler shifted with respect to the ion rest frame) and in the rest frame of the H_3^+ ions ($\tilde{\nu}_0$) with estimated rms uncertainties (in parentheses) in the final digits, for statistical and systematic uncertainties combined. The larger uncertainty of the present frequencies relative to previous experiments arises primarily from the Doppler shift affecting our measurements, which employ a fast stored ion beam. The uncertainty of the Doppler shift is dominated by the uncertainty of the length of the nominal ion orbit path (see Sec. IV A). This uncertainty is absent in the absorption cell measurement of Ref. [36] and the ion trap action spectroscopy of Ref. [41]. As discussed in the text, this systematic uncertainty can be substantially reduced in future measurements by referencing the Doppler shift to previously known transition frequencies.

I	Assignment	This experiment		Previous experiments	Theory [64]
		$\tilde{\nu}_D$	$\tilde{\nu}_0$	$\tilde{\nu}_0$	$\tilde{\nu}_0$
1/2 (para)	$00^0(1, 1) \rightarrow 31^1(0, 1)$	11 185.759(13)	11 258.847(105)	11 258.975(10) [41]	11 258.975(10)
3/2 (ortho)	$00^0(1, 0) \rightarrow 31^1(1, 0)$	11 244.477(13)	11 317.949(105)	11 318.084(10) [36]	11 318.082(10)
Difference		58.718(18)	59.102(19)	59.109(14)	59.107(14)

Schottky pickup electrode, and the trajectory length of the ion beam orbit. The orbital circumference is inferred from the geometry of the storage ring's ion optical lattice, resulting in a relatively large uncertainty of 5 cm for the nominal path length of 35.12 m. This translates into an uncertainty of 9×10^{-6} for the Doppler correction factor and $\sim 0.1 \text{ cm}^{-1}$ for the Doppler-corrected frequencies, dominating the uncertainty of the measurement.

Based on Table II, our rest-frame frequencies $\tilde{\nu}_0$ agree within 1.3σ with the experimental values reported by Kreckel *et al.* (for the para transition, [41]) and Gottfried *et al.* (for the ortho transition, [36]), as well as with the semiempirical energy levels of Bowesman *et al.* [64], obtained via the MARVEL (measured active rotational-vibrational energy levels) procedure [91], which was used to improve calculated line lists using a network of previously measured transitions.

The excellent agreement regarding the difference between the two observed transition frequencies indicates that accurate spectrometry is possible by referencing our setup to previously measured transition frequencies and thus eliminating the largest systematic uncertainty of the orbit trajectory length. In particular, instead of calculating the rest-frame transition frequency based on the nominal orbital path length, we can use the measured rest-frame frequencies of Kreckel *et al.* and Gottfried *et al.* to determine from our measured laboratory frequencies the Doppler shift factor of 1.006 5458(22) and thereby infer the path length for the precisely measured ion revolution frequency. This results in an orbital length of 35.19(1) m in fair agreement with the previously assumed value of 35.12(5) m. Moreover, the momentum spread of the ion beam can be extracted from the width of the fitted Gaussian, yielding a value of $\Delta p/p = 2.3(1) \times 10^{-4}$, which is in the expected range for an electron-cooled ion beam.

In addition to the frequency uncertainties discussed above, the amplitude of the measured signal is subject to several systematic effects. Laser power was monitored continuously at the exit from the overlap region and found to be stable within a few percent in the course of a scan. This also rules out major overlap changes, as the laser beam path is confined by narrow apertures and the ion beam position is stabilized by electron cooling. Run-to-run variations in other quantities, like the number of injected ions, partially motivate the per-injection normalization scheme introduced above. Typical measurement campaigns at the CSR require the ion-optical lattice and detector response to be stable for hours to days, and signal variations on a time scale of seconds due to ion beam position variations or detector efficiencies can therefore be ruled out.

B. Time evolution of the signal and inferred DR rate enhancement for excited states of H_3^+

Throughout the next sections, we will try to infer information on relative DR enhancements in individual states by comparing the measured time-dependent signal with populations from the simulation of Sec. II; such conclusions are therefore inherently conditional on the assumptions underlying the model.

Regarding Eq. (5), it should be noted that the gated neutral rates $R_{\text{e-on}}(\nu)$ and $R_{\text{e-off}}$ refer to the average over the 4-s-long

laser exposure period. Both rates can also be obtained for subwindows $t \cdots t + \Delta t$ of this time interval, yielding the time-dependent signal

$$S_{\text{DR}}(\nu, t, \Delta t) = \frac{\langle R^{\text{DR}}(\nu) \rangle_{t \cdots t + \Delta t}}{R_0^{\text{DR}}} = \frac{\langle R_{\text{e-on}}(\nu) - R_{\text{e-off}} \rangle_{t \cdots t + \Delta t}}{R_{\text{e-on}}^{\text{pre}} - R_{\text{e-off}}}. \quad (7)$$

Splitting the DR signal during the laser exposure into time slices as described in Eq. (7), we can analyze the time dependence of optical pumping into excited states of H_3^+ with an enhanced DR rate. For the fitted amplitudes A_R of the Gaussian fits to the time-sliced signals, the observed time dependence during laser exposure is shown in Fig. 6. At both spin symmetries, the spectroscopic signal increases within the first second, similar to the increase of the population in all vibrational states predicted by the simulations in Sec. II [Fig. 3(b)]. After the initial rise, the observed time dependence is remarkably different for the two spin symmetries. While for the ortho transition the signal slowly decreases after a maximum reached at ~ 1 s, it remains at a high level for the para transition, with even a slow further increase.

The behavior for the ortho line agrees quite well with the time dependence of the population in all vibrationally excited states obtained in the simulation. This time dependence is also shown in Fig. 6(b) by the red line, obtained by multiplying the simulation results with a constant factor that minimizes χ^2 between the simulated population evolution in all vibrationally excited states and the measured signal amplitudes A_R . The clear decay of the signal after 1 s of laser exposure coincides with the expected decay of vibrationally excited states. In contrast, for the para transition in Fig. 6(a), the time dependence of the observed signal clearly differs from that of the simulation (red line).

Before interpreting the unexpected para time dependence through relative variations in the DR rate for different states, we consider alternative explanations.

Uncertainties in the Einstein coefficients were tested directly by simulating the vibrationally excited population assuming different values of the laser absorption rates. Here, we scaled these rates, proportional to the Einstein B coefficients of the respective target transitions, with a factor η varied between 1.5 and 0.25, as shown in Fig. 6. For the ortho transition, the observed time dependence can be well represented by these simulations with η in the range between 0.5 and 1. Contrarily, no variation of η brings the time dependence into agreement with the observed signal for the para transition.

Imperfect laser-ion overlap and residual systematic effects would be expected to affect the para and ortho measurements similarly, given the identical experimental configuration used for both transitions, and therefore cannot easily account for the qualitative difference between them. Incompleteness of the underlying line list could in principle affect the simulated population dynamics, but we consider the vibrational lifetimes as reliable [59], and we would not expect them to produce a spin-symmetry-specific discrepancy. We therefore consider enhanced DR rates for rotationally excited states the most plausible explanation for the observed plateau in the para signal.

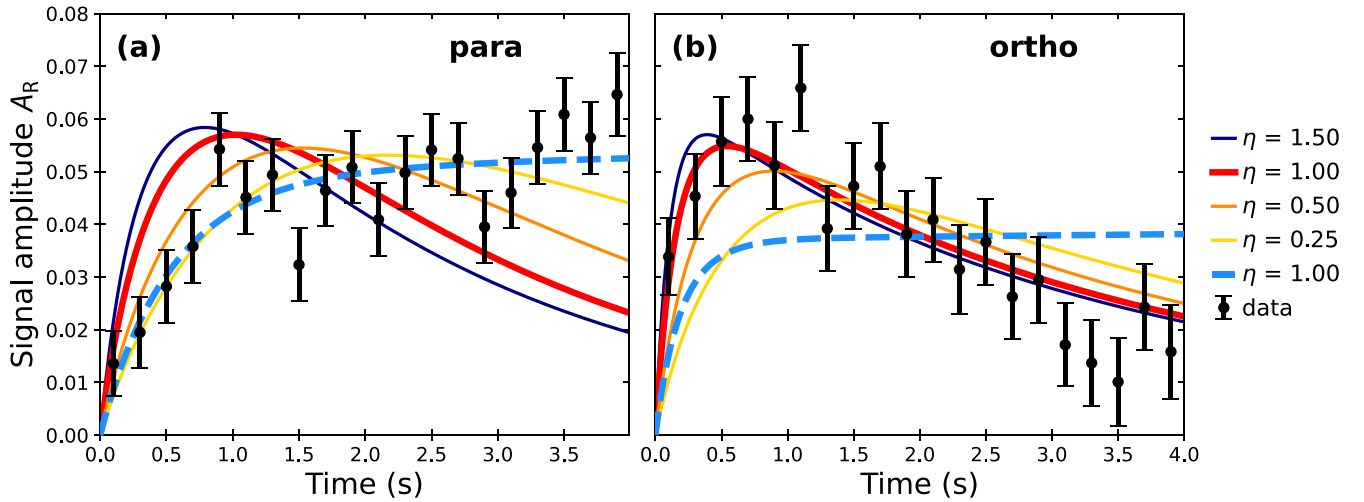


FIG. 6. Time dependence of the amplitude A_R fitted to the signal $S_{DR}(\nu, t, \Delta t)$ of Eq. (7) for intervals $\Delta t = 0.2$ s shown as functions of the interval midpoints $t + \Delta t/2$, during laser exposure on the (a) para and (b) ortho spectral lines. Red thick solid lines: scaled populations of all vibrationally excited states from the simulation of Sec. II. Colored thin solid lines: scaled simulated populations assuming laser transition rates increased or decreased by the factor η , as indicated. Blue dashed lines: simulated population of all vibrationally and rotationally excited H_3^+ states. In all cases, the simulated populations have been scaled to minimize the χ^2 value to the measured signal amplitude A_R .

C. Optical pumping of vibrationally and rotationally excited levels

The time dependence of the spectroscopic signal for the ortho transition indicates that the model for the population increase in all vibrationally excited levels captures the experimental conditions fairly well. Considering the relevant level lifetimes for vibrational as opposed to rotational excitation, the overall time structure of the ortho signal strongly hints at *vibrationally* excited states as the origin of the enhanced DR signal, since the lifetimes of low-lying rotational states exceed the measurement interval by orders of magnitude, as seen in the simulation results of Fig. 3(c).

In the long-time limit, most of the population is predicted to become trapped in the very long lived $(J, G) = (3, 3)$ state. This state is the only excited H_3^+ state that has been observed in interstellar space to date, more specifically in sightlines toward the galactic center [92], and it has been used to infer important astrophysical parameters for this special environment [93], under the assumption that its DR rate coefficient is not substantially different from the rate coefficient of the ground state. The agreement of our results for the ortho state with the simulated time dependence of vibrationally excited levels is consistent with the DR rate coefficient of the rotationally excited state not being significantly enhanced, within the framework of our population model. In the opposite case, the observed signal would remain high at longer laser exposure times, when more and more population is pumped into the $(3, 3)$ state. This is the first qualitative experimental evidence on the DR rate coefficient of this metastable rotationally excited state of H_3^+ .

For the para transition, on the other hand, vibrational excitation alone cannot explain the DR signal enhancement. A plateau is forming after 1 s of laser exposure, indicating that in this case the slow buildup of long-lived rotationally excited states contributes to the enhanced DR signal. The dashed blue line in Fig. 6(a) represents the time evolution of all

excited-state populations, both vibrationally and *rotationally* excited, which clearly reflects the experimental data points better than the curve of the vibrationally excited states only. According to our simulation [Fig. 3(b)], the population in this case is expected to be dominated by the $(J, G) = (2, 2)$ and $(2, 1)$ rotationally excited states after 2 s of laser exposure. On this basis, we infer that the DR rate coefficient of at least one of these states would need to be significantly enhanced compared to the ground state to reproduce the observed signal plateau. This may have interesting implications for the chemistry of the galactic center, as the absence of the $(2, 2)$ state has been interpreted as an indicator for low particle densities [93], while our results open up the possibility that it may be explained by a faster electron recombination rate.

As the internal excitation of interstellar H_3^+ has been a recurring puzzle in astrophysical studies [94], state-specific DR rates are crucial for a better understanding of many interstellar environments. Our proof-of-principle measurements demonstrate that it is possible to address and manipulate individual rotational states inside the storage ring and for the first time infer information on their relative DR rate coefficients. More detailed studies are foreseen in the future.

V. CONCLUSION AND OUTLOOK

The successful performance of the initial excitation step of the multicolor scheme developed by Znotins *et al.* [80] marks a significant milestone toward action spectroscopy of highly excited H_3^+ states above $20\,000\text{ cm}^{-1}$. Specifically, the present work validates two prerequisites for the full multicolor scheme: It demonstrates that the proposed optical pumping pathway populates the intended excited states at the predicted frequencies and it shows that the achievable degree of state preparation is sufficient to produce a clearly resolved signal under realistic CSR operating conditions.

By laser excitation to a target state already above the barrier to linearity, the subsequent radiative cascade allowed

us to accumulate a significant fraction of stored H_3^+ ions in metastable excited states. The fraction was substantial enough to be detected by an increase of the electron recombination rate of a stored H_3^+ ion beam. Through the spectral resolution in the laser excitation step, the two nuclear spin symmetries of H_3^+ could be addressed separately. Our simulations based on the extensive linelist by Bowesman *et al.* [64], predicting the time dependence of the optical pumping process, can be accommodated with the observations if simple assumptions are made on the enhancement of the electron recombination rate for different subsets of excited states. Showing good agreement with the time evolution of the simulated populations under laser exposure, our comparison of the measured signal time dependence with simulated population dynamics is consistent with significant enhancements of the electron recombination rate for vibrationally excited states of both nuclear spin symmetries. As shown in Sec. IV C, the conclusions can even be extended further to long-lived rotational states within the vibrational ground level, where the comparison indicates enhanced electron recombination rates specifically for the para, but not for the ortho symmetry.

While action spectroscopy of molecular ions has been extensively performed at ion storage rings, it has thus far been limited to the detection of neutral products from photodissociation processes [95–99]. This experiment marks the first use of electron-ion recombination as a detection method in a molecular spectroscopy scheme. We demonstrate, by the use of laser population pumping, that the H_3^+ electron recombination rate coefficient is sensitive to the individual quantum state of the ion, with a pronounced increase inferred upon vibrational as well as rotational excitation. Indeed, the experiment again highlights the significant role of rotational excitation in the dissociative recombination of H_3^+ , recently addressed in joint experimental and theoretical studies for the DR of deuterated triatomic hydrogen ions H_2D^+ [69] and D_2H^+ [68]. Going beyond these studies, the present work indicates enhanced DR rates specifically for at least one

of the long-lived $(J, G) = (2, 2)$ and $(2, 1)$ para rotational states, demonstrating the power of state-selective investigations through optical pumping and opening up more detailed studies for the near future.

Having validated the pumping concept and state preparation efficiency, the principal remaining experimental bottleneck for the full multicolor scheme is the addition of the second, tunable excitation laser required to reach the target energy range above $20\,000\text{ cm}^{-1}$. With the first of these milestones now in place, the full spectroscopy scheme for highly excited H_3^+ states can be pursued in the near future. The high-resolution collinear laser setup at the CSR, showcased by the present measurement, is presently being complemented by two additional lasers to enable efficient two-step excitation and subsequent photodissociation. While the first laser will be locked at the transition frequencies measured in this work, the second tunable laser will scan for transitions toward very highly excited states above $20\,000\text{ cm}^{-1}$, where theoretical predictions carry substantial uncertainty. The complete implementation of this scheme will be a great stride toward bridging the huge energetic gap to the dissociation limit of H_3^+ , marking a significant advance in the exploration of this fundamental molecular ion. Moreover, the multicolor scheme will allow for *in situ* laser diagnostics of individual rotational states inside the CSR, paving the way toward state-selected DR measurements with H_3^+ .

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DATA AVAILABILITY

The data that support the findings of this article are openly available in the Edmond repository at [100].

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- [1] I. Manai, R. Horchani, H. Lignier, P. Pillet, D. Comparat, A. Fioretti, and M. Allegrini, Rovibrational cooling of molecules by optical pumping, *Phys. Rev. Lett.* **109**, 183001 (2012).
 - [2] G. Quémener and P. S. Julienne, Ultracold molecules under control!, *Chem. Rev.* **112**, 4949 (2012).
 - [3] J. M. Hutson, Ultracold chemistry, *Science* **327**, 788 (2010).
 - [4] N. J. Fitch and M. R. Tarbutt, Laser-cooled molecules, *Adv. At. Mol. Opt. Phys.* **70**, 157 (2021).
 - [5] I. Kozyryev, L. Baum, K. Matsuda, B. L. Augenbraun, L. Anderegg, A. P. Sedlack, and J. M. Doyle, Sisyphus laser cooling of a polyatomic molecule, *Phys. Rev. Lett.* **118**, 173201 (2017).
 - [6] L. Baum, N. B. Vilas, C. Hallas, B. L. Augenbraun, S. Raval, D. Mitra, and J. M. Doyle, 1D magneto-optical trap of polyatomic molecules, *Phys. Rev. Lett.* **124**, 133201 (2020).
 - [7] Y. Zeng, A. Jadbabaie, A. N. Patel, P. Yu, T. C. Steimle, and N. R. Hutzler, Optical cycling in polyatomic molecules with complex hyperfine structure, *Phys. Rev. A* **108**, 012813 (2023).
 - [8] J. B. Dragan, I. O. Antonov, and B. C. Odom, Features of molecular structure beneficial for optical pumping, *Phys. Rev. A* **107**, 033110 (2023).
 - [9] M. V. Ivanov, T.-C. Jagau, G.-Z. Zhu, E. R. Hudson, and A. I. Krylov, In search of molecular ions for optical cycling: A difficult road, *Phys. Chem. Chem. Phys.* **22**, 17075 (2020).
 - [10] C.-Y. Lien, C. M. Seck, Y.-W. Lin, J. H. V. Nguyen, D. A. Tabor, and B. C. Odom, Broadband optical cooling of molecular rotors from room temperature to the ground state, *Nat. Commun.* **5**, 4783 (2014).
 - [11] P. R. Stollenwerk, B. C. Odom, D. L. Kokkin, and T. Steimle, Electronic spectroscopy of a cold SiO^+ sample: Implications for optical pumping, *J. Mol. Spectrosc.* **332**, 26 (2017).
 - [12] P. R. Stollenwerk, M. G. Kokish, A. G. S. de Oliveira-Filho, F. R. Ornellas, and B. C. Odom, Optical pumping of TeH^+ : Implications for the search for varying m_p/m_e , *Atoms* **6**, 53 (2018).
 - [13] T. Schneider, B. Roth, H. Duncker, I. Ernsting, and S. Schiller, All-optical preparation of molecular ions

- in the rovibrational ground state, *Nat. Phys.* **6**, 275 (2010).
- [14] S. Alighanbari, M. G. Hansen, V. I. Korobov, and S. Schiller, Rotational spectroscopy of cold and trapped molecular ions in the Lamb-Dicke regime, *Nat. Phys.* **14**, 555 (2018).
- [15] S. Alighanbari, G. S. Giri, F. L. Constantin, V. I. Korobov, and S. Schiller, Precise test of quantum electrodynamics and determination of fundamental constants with HD^+ ions, *Nature (London)* **581**, 152 (2020).
- [16] R. von Hahn, A. Becker, F. Berg, K. Blaum, C. Breitenfeldt, H. Fadil, F. Fellenberger, M. Froese, S. George, J. Göck, *et al.*, The cryogenic storage ring CSR, *Rev. Sci. Instrum.* **87**, 063115 (2016).
- [17] J. J. Thomson, Bakerian Lecture: Rays of positive electricity, *Proc. R. Soc. Lond. A* **89**, 1 (1913).
- [18] T. Oka, Observation of the infrared spectrum of H_3^+ , *Phys. Rev. Lett.* **45**, 531 (1980).
- [19] A. Carrington, J. Buttenshaw, and R. Kennedy, Observation of the infrared spectrum of H_3^+ at its dissociation limit, *Mol. Phys.* **45**, 753 (1982).
- [20] F. Kemp, C. E. Kirk, and I. R. McNab, The infrared predissociation spectrum of H_3^+ , *Philos. Trans. R. Soc. Lond. Ser. A* **358**, 2403 (2000).
- [21] E. Herbst and W. Klemperer, The formation and depletion of molecules in dense interstellar clouds, *Astrophys. J.* **185**, 505 (1973).
- [22] W. D. Watson, The rate of formation of interstellar molecules by ion-molecule reactions, *Astrophys. J.* **183**, L17 (1973).
- [23] T. Oka, H_3^+ , the ideal probe for in situ measurement of the Galactic cosmic rays, *Philos. Trans. R. Soc. A* **377**, 20180402 (2019).
- [24] I. Labbé, P. van Dokkum, E. Nelson, R. Bezanson, K. A. Suess, J. Leja, G. Brammer, K. Whitaker, E. Mathews, M. Stefanon, and B. Wang, A population of red candidate massive galaxies ~ 600 Myr after the Big Bang, *Nature (London)* **616**, 266 (2023).
- [25] A. Ferrara, A. Pallottini, and P. Dayal, On the stunning abundance of super-early, luminous galaxies revealed by JWST, *Mon. Not. R. Astron. Soc.* **522**, 3986 (2023).
- [26] A. Pandey, O. Dulieu, and N. Bouloufa-Maafa, An alternate pathway for H_2 formation in the early universe: A physical process to account for the presence and coevolution of the luminous galaxies and supermassive black holes at the high redshifts, *arXiv:2603.08662*.
- [27] M. Quack, Detailed symmetry selection rules for reactive collisions, *Mol. Phys.* **34**, 477 (1977).
- [28] C. M. Lindsay and B. J. McCall, Comprehensive evaluation and compilation of H_3^+ spectroscopy, *J. Mol. Spectrosc.* **210**, 60 (2001).
- [29] T. R. Geballe and T. Oka, Detection of H_3^+ in interstellar space, *Nature (London)* **384**, 334 (1996).
- [30] B. J. McCall, T. R. Geballe, K. H. Hinkle, and T. Oka, Detection of H_3^+ in the diffuse interstellar medium toward Cygnus OB2 No. 12, *Science* **279**, 1910 (1998).
- [31] P. Drossart, J.-P. Maillard, J. Caldwell, S. J. Kim, J. K. G. Watson, W. A. Majewski, J. Tennyson, S. Miller, S. K. Atreya, J. T. Clarke, J. H. Waite, and R. Wagoner, Detection of H_3^+ on Jupiter, *Nature (London)* **340**, 539 (1989).
- [32] T. R. Geballe, M.-F. Jagod, and T. Oka, Detection of H_3^+ infrared emission lines in Saturn, *Astrophys. J. Lett.* **408**, L109 (1993).
- [33] T. R. Geballe, M. Goto, T. Usuda, T. Oka, and B. J. McCall, The interstellar medium of IRAS 08572+3915 NW: H_3^+ and warm high-velocity CO, *Astrophys. J.* **644**, 907 (2006).
- [34] B. J. McCall, A. J. Huneycutt, R. J. Saykally, T. R. Geballe, N. Djuric, G. H. Dunn, J. Semaniak, O. Novotny, A. Al-Khalili, A. Ehlerding, F. Hellberg, S. Kalhori, A. Neau, R. Thomas, F. Österdahl, and M. Larsson, An enhanced cosmic-ray flux towards ζ Persei inferred from a laboratory study of the $\text{H}_3^+ \text{-e}^-$ recombination rate, *Nature (London)* **422**, 500 (2003).
- [35] S. Miller, J. Tennyson, T. R. Geballe, and T. Stallard, Thirty years of H_3^+ astronomy, *Rev. Mod. Phys.* **92**, 035003 (2020).
- [36] J. L. Gottfried, B. J. McCall, and T. Oka, Near-infrared spectroscopy of H_3^+ above the barrier to linearity, *J. Chem. Phys.* **118**, 10890 (2003).
- [37] R. Röhse, W. Kutzelnigg, R. Jaquet, and W. Klopper, Potential energy surface of the H_3^+ ground state in the neighborhood of the minimum with microhartree accuracy and vibrational frequencies derived from it, *J. Chem. Phys.* **101**, 2231 (1994).
- [38] J. L. Gottfried, Near-infrared spectroscopy of H_3^+ above the barrier to linearity, *Phil. Trans. R. Soc. A* **364**, 2917 (2006).
- [39] S. Schlemmer, T. Kuhn, E. Lescop, and D. Gerlich, Laser excited N_2^+ in a 22-pole ion trap, *Int. J. Mass Spectrom.* **185–187**, 589 (1999).
- [40] J. Mikosch, H. Kreckel, R. Wester, R. Plašil, J. Glosík, D. Gerlich, D. Schwalm, and A. Wolf, Action spectroscopy and temperature diagnostics of H_3^+ by chemical probing, *J. Chem. Phys.* **121**, 11030 (2004).
- [41] H. Kreckel, D. Bing, S. Reinhardt, A. Petrigani, M. Berg, and A. Wolf, Chemical probing spectroscopy of H_3^+ above the barrier to linearity, *J. Chem. Phys.* **129**, 164312 (2008).
- [42] M. Berg, A. Wolf, and A. Petrigani, Visible transitions from ground state H_3^+ measured with high-sensitivity action spectroscopy, *Philos. Trans. R. Soc. A* **370**, 5028 (2012).
- [43] M. Pavanello, L. Adamowicz, A. Alijah, N. F. Zobov, I. I. Mízus, O. L. Polyansky, J. Tennyson, T. Szidarovszky, A. G. Császár, M. Berg, A. Petrigani, and A. Wolf, Precision measurements and computations of transition energies in rotationally cold triatomic hydrogen ions up to the midvisible spectral range, *Phys. Rev. Lett.* **108**, 023002 (2012).
- [44] P. Jusko, C. Konietzko, S. Schlemmer, and O. Asvany, Frequency comb assisted measurement of fundamental transitions of cold H_3^+ , H_2D^+ and D_2H^+ , *J. Mol. Spectrosc.* **319**, 55 (2016).
- [45] M. Berblinger, E. Pollak, and C. Schlier, Bound states embedded in the continuum of H_3^+ , *J. Chem. Phys.* **88**, 5643 (1988).
- [46] J. M. Gomez Llorente and E. Pollak, A classical trajectory study of the photodissociation spectrum of H_3^+ , *J. Chem. Phys.* **90**, 5406 (1989).
- [47] J. R. Henderson and J. Tennyson, Calculated spectrum for near-dissociation H_3^+ : A first attempt, *Mol. Phys.* **89**, 953 (1996).
- [48] G. D. Carney and R. N. Porter, H_3^+ : Geometry dependence of electronic properties, *J. Chem. Phys.* **60**, 4251 (1974).
- [49] G. D. Carney and R. N. Porter, H_3^+ : *Ab initio* calculation of the vibration spectrum, *J. Chem. Phys.* **65**, 3547 (1976).

- [50] J. Tennyson and B. T. Sutcliffe, The *ab initio* calculation of the vibrational-rotational spectrum of triatomic systems in the close-coupling approach, with KCN and H₂Ne as examples, *J. Chem. Phys.* **77**, 4061 (1982).
- [51] B. T. Sutcliffe and J. Tennyson, A generalized approach to the calculation of ro-vibrational spectra of triatomic molecules, *Mol. Phys.* **58**, 1053 (1986).
- [52] S. Miller and J. Tennyson, First principles calculation of the molecular constants of H₃⁺, H₂D⁺, D₂H⁺, and D₃⁺, *J. Mol. Spectrosc.* **126**, 183 (1987).
- [53] W. Meyer, P. Botschwina, and P. Burton, *Ab initio* calculation of near-equilibrium potential and multipole moment surfaces and vibrational frequencies of H₃⁺ and its isotopomers, *J. Chem. Phys.* **84**, 891 (1986).
- [54] L. Kao, T. Oka, S. Miller, and J. Tennyson, A table of astronomically important ro-vibrational transitions for the H₃⁺ molecular ion, *Astrophys. J. Suppl. Ser.* **77**, 317 (1991).
- [55] Z. Bačić and J. C. Light, Theoretical methods for rovibrational states of floppy molecules, *Annu. Rev. Phys. Chem.* **40**, 469 (1989).
- [56] L. Neale, S. Miller, and J. Tennyson, Spectroscopic properties of the H₃⁺ molecule: A new calculated line list, *Astrophys. J.* **464**, 516 (1996).
- [57] B. M. Dinelli, O. L. Polyansky, and J. Tennyson, Spectroscopically determined Born-Oppenheimer and adiabatic surfaces for H₃⁺, H₂D⁺, D₂H⁺, and D₃⁺, *J. Chem. Phys.* **103**, 10433 (1995).
- [58] S. C. O. Glover and D. W. Savin, Is H₃⁺ cooling ever important in primordial gas? *Mon. Not. R. Astron. Soc.* **393**, 911 (2009).
- [59] H. Kreckel, S. Krohn, L. Lammich, M. Lange, J. Levin, M. Scheffel, D. Schwalm, J. Tennyson, Z. Vager, R. Wester, A. Wolf, and D. Zajfman, Vibrational and rotational cooling of H₃⁺, *Phys. Rev. A* **66**, 052509 (2002).
- [60] C. Hill, S. N. Yurchenko, and J. Tennyson, Temperature-dependent molecular absorption cross sections for exoplanets and other atmospheres, *Icarus* **226**, 1673 (2013).
- [61] A. Petignani, M. H. Berg, F. Grussie, A. Wolf, I. I. Mizus, O. L. Polyansky, J. Tennyson, N. F. Zobov, M. Pavanello, and L. Adamowicz, Communication: Visible line intensities of the triatomic hydrogen ion from experiment and theory, *J. Chem. Phys.* **141**, 241104 (2014).
- [62] M. Pavanello, L. Adamowicz, A. Alijah, N. F. Zobov, I. I. Mizus, O. L. Polyansky, J. Tennyson, T. Szidarovszky, and A. G. Császár, Calibration-quality adiabatic potential energy surfaces for H₃⁺ and its isotopologues, *J. Chem. Phys.* **136**, 184303 (2012).
- [63] I. I. Mizus, A. Alijah, N. F. Zobov, L. Lodi, A. A. Kyuberis, S. N. Yurchenko, J. Tennyson, and O. L. Polyansky, ExoMol molecular line lists—XX. A comprehensive line list for H₃⁺, *Mon. Not. R. Astron. Soc.* **468**, 1717 (2017).
- [64] C. A. Bowesman, I. I. Mizus, N. F. Zobov, O. L. Polyansky, J. Sarka, B. Poirier, M. Pezzella, S. N. Yurchenko, and J. Tennyson, Exomol line lists—L: High-resolution line lists of H₃⁺, H₂D⁺, D₂H⁺, and D₃⁺, *Mon. Not. R. Astron. Soc.* **519**, 6333 (2023).
- [65] H. Kreckel, M. Motsch, J. Mikosch, J. Glosík, R. Plašil, S. Altevogt, V. Andrianarijaona, H. Buhr, J. Hoffmann, L. Lammich, *et al.*, High-resolution dissociative recombination of cold H₃⁺ and first evidence for nuclear spin effects, *Phys. Rev. Lett.* **95**, 263201 (2005).
- [66] H. Kreckel, O. Novotný, K. N. Crabtree, H. Buhr, A. Petignani, B. A. Tom, R. D. Thomas, M. H. Berg, D. Bing, M. Grieser, C. Krantz, M. Lestinsky, M. B. Mendes, C. Nordhorn, R. Repnow, J. Stützel, A. Wolf, and B. J. McCall, High-resolution storage-ring measurements of the dissociative recombination of H₃⁺ using a supersonic expansion ion source, *Phys. Rev. A* **82**, 042715 (2010).
- [67] A. Petignani, S. Altevogt, M. H. Berg, D. Bing, M. Grieser, J. Hoffmann, B. Jordon-Thaden, C. Krantz, M. B. Mendes, O. Novotný, S. Novotny, D. A. Orlov, R. Repnow, T. Sorg, J. Stützel, A. Wolf, H. Buhr, H. Kreckel, V. Kokoouline, and C. H. Greene, Resonant structure of low-energy H₃⁺ dissociative recombination, *Phys. Rev. A* **83**, 032711 (2011).
- [68] A. Znotins, A. Faure, C. H. Greene, M. Grieser, F. Grussie, L. W. Isberner, Á. Kálosi, V. Kokoouline, D. Müll, D. Paul, M. Pezzella, D. W. Savin, S. Schippers, J. Tennyson, A. Wolf, O. Novotný, and H. Kreckel, Electron recombination of rotationally cold D₂H⁺ ions, *Nat. Commun.* **16**, 7738 (2025).
- [69] A. Znotins, A. Faure, C. H. Greene, M. Grieser, F. Grussie, L. W. Isberner, Á. Kálosi, V. Kokoouline, D. Müll, D. Paul, M. Pezzella, D. W. Savin, S. Schippers, J. Tennyson, A. Wolf, O. Novotný, and H. Kreckel, Dissociative electron recombination and rotational cooling of the deuterated triatomic hydrogen ions H₂D⁺ and D₂H⁺, *Phys. Rev. A* **112**, 052819 (2025).
- [70] S. Krohn, H. Kreckel, L. Lammich, M. Lange, J. Levin, D. Schwalm, D. Strasser, R. Wester, A. Wolf, and D. Zajfman, Electron induced vibrational deexcitation of the molecular ions H₂⁺ and D₂⁺, in *Dissociative Recombination of Molecular Ions with Electrons*, edited by S. L. Guberman (Springer US, Boston, MA, 2003), pp. 127–138.
- [71] H. Buhr, H. B. Pedersen, S. Altevogt, V. M. Andrianarijaona, H. Kreckel, L. Lammich, S. Novotny, D. Strasser, J. Hoffmann, M. Lange, M. Lestinsky, M. B. Mendes, M. Motsch, O. Novotný, D. Schwalm, X. Urbain, D. Zajfman, and A. Wolf, Electron collisions with ⁴He₂⁺ at the TSR, *J. Phys.: Conf. Ser.* **192**, 012013 (2009).
- [72] A. Petignani, W. J. van der Zande, P. C. Cosby, F. Hellberg, R. D. Thomas, and M. Larsson, Vibrationally resolved rate coefficients and branching fractions in the dissociative recombination of O₂⁺, *J. Chem. Phys.* **122**, 014302 (2005).
- [73] H. Hus, F. Youssif, A. Sen, and J. B. A. Mitchell, Merged-beam studies of the dissociative recombination of H₃⁺ ions with low internal energy, *Phys. Rev. A* **38**, 658 (1988).
- [74] M. Larsson, B. McCall, and A. Orel, The dissociative recombination of H₃⁺—A saga coming to an end? *Chem. Phys. Lett.* **462**, 145 (2008).
- [75] V. Kokoouline, C. H. Greene, and B. D. Esry, Mechanism for the destruction of H₃⁺ ions by electron impact, *Nature (London)* **412**, 891 (2001).
- [76] V. Kokoouline and C. H. Greene, Theory of dissociative recombination of D_{3h} triatomic ions applied to H₃⁺, *Phys. Rev. Lett.* **90**, 133201 (2003).
- [77] S. F. dos Santos, V. Kokoouline, and C. H. Greene, Dissociative recombination of H₃⁺ in the ground and excited vibrational states, *J. Chem. Phys.* **127**, 124309 (2007).
- [78] C. Jungen and S. T. Pratt, Jahn-Teller interactions in the dissociative recombination of H₃⁺, *Phys. Rev. Lett.* **102**, 023201 (2009).
- [79] B. M. Dinelli, S. Miller, and J. Tennyson, Bands of H₃⁺ up to 4ν₂: Rovibrational transitions from first

- principles calculations, *J. Mol. Spectrosc.* **153**, 718 (1992).
- [80] A. Znotins, F. Grussie, A. Wolf, X. Urbain, and H. Kreckel, An approach for multi-color action spectroscopy of highly excited states of H_3^+ , *J. Mol. Spectrosc.* **378**, 111476 (2021).
- [81] X. Urbain, A. Dochain, R. Marion, T. Launoy, and J. Loreau, Photodissociation as a probe of the H_3^+ avoided crossing seam, *Philos. Trans. R. Soc. A* **377**, 20180399 (2019).
- [82] L. Berger, F. Grussie, F. Nuesslein, O. Novotný, A. Znotins, J. Fréreau, X. Urbain, and H. Kreckel, Characterization of a simple gas expansion ion source for intense pulses of subthermal molecular ions, *Rev. Sci. Instrum.* **96**, 013301 (2025).
- [83] F. Merkt, K. Höveler, and J. Deiglmayr, Reactions of H_2 , HD, and D_2 with H_2^+ , HD^+ , and D_2^+ : Product-channel branching ratios and simple models, *J. Phys. Chem. Lett.* **13**, 864 (2022).
- [84] H. Kreckel, J. Tennyson, D. Schwalm, D. Zajfman, and A. Wolf, Rovibrational relaxation model for H_3^+ , *New J. Phys.* **6**, 151 (2004).
- [85] H. Poth, Electron cooling: Theory, experiment, application, *Phys. Rep.* **196**, 135 (1990).
- [86] D. Paul, M. Grieser, F. Grussie, R. von Hahn, L. W. Isberner, Á. Kálosi, C. Krantz, H. Kreckel, D. Müll, D. A. Neufeld, D. W. Savin, S. Schippers, P. Wilhelm, A. Wolf, M. G. Wolfire, and O. Novotný, Experimental determination of the dissociative recombination rate coefficient for rotationally cold CH^+ and its implications for diffuse cloud chemistry, *Astrophys. J.* **939**, 122 (2022).
- [87] N. Jain, Á. Kálosi, F. Nuesslein, D. Paul, P. Wilhelm, S. G. Ard, M. Grieser, R. von Hahn, M. C. Heaven, E. Miliordos, D. Maffucci, N. S. Shuman, A. A. Viggiano, A. Wolf, and O. Novotný, Near-thermo-neutral electron recombination of titanium oxide ions, *J. Chem. Phys.* **158**, 144305 (2023).
- [88] Á. Kálosi, L. Gamer, M. Grieser, R. von Hahn, L. W. Isberner, J. I. Jäger, H. Kreckel, D. A. Neufeld, D. Paul, D. W. Savin, S. Schippers, V. C. Schmidt, A. Wolf, M. G. Wolfire, and O. Novotný, Dissociative recombination of rotationally cold OH^+ and its implications for the cosmic ray ionization rate in diffuse clouds, *Astrophys. J. Lett.* **955**, L26 (2023).
- [89] Á. Kálosi, M. Grieser, L. W. Isberner, H. Kreckel, Å. Larson, D. A. Neufeld, A. E. Orel, D. Paul, D. W. Savin, S. Schippers, V. C. Schmidt, A. Wolf, M. G. Wolfire, and O. Novotný, Dissociative recombination of rotationally cold ArH^+ , *Phys. Rev. A* **110**, 022816 (2024).
- [90] A. E. Siegman, *Lasers* (University Science Books, Mill Valley, CA, 1986).
- [91] T. Furtenbacher, A. G. Császár, and J. Tennyson, MARVEL: Measured active rotational-vibrational energy levels, *J. Mol. Spectrosc.* **245**, 115 (2007).
- [92] M. Goto, B. J. McCall, T. R. Geballe, T. Usuda, N. Kobayashi, H. Terada, and T. Oka, Absorption line survey of H_3^+ toward the Galactic center sources I. GCS 3-2 and GC IRS3, *Publ. Astron. Soc. Jpn.* **54**, 951 (2002).
- [93] T. Oka, T. R. Geballe, M. Goto, T. Usuda, Benjamin, J. McCall, and N. Indriolo, The central 300 pc of the Galaxy probed by infrared spectra of H_3^+ and CO. I. Predominance of warm and diffuse gas and high H_2 ionization rate, *Astrophys. J.* **883**, 54 (2019).
- [94] J. Le Bourlot, E. Roueff, F. Le Petit, F. Kehrein, A. Oetjens, and H. Kreckel, Understanding the temperatures of H_3^+ and H_2 in diffuse interstellar sightlines, *Mol. Phys.* **122**, e2182612 (2024).
- [95] U. Hechtfisher, Z. Amitay, P. Forck, M. Lange, J. Linkemann, M. Schmitt, U. Schramm, D. Schwalm, R. Wester, D. Zajfman, and A. Wolf, Near-threshold photodissociation of cold CH^+ in a storage ring, *Phys. Rev. Lett.* **80**, 2809 (1998).
- [96] A. Hirota, R. Igosawa, N. Kimura, S. Kuma, K. C. Chartkunchand, P. M. Mishra, M. Lindley, T. Yamaguchi, Y. Nakano, and T. Azuma, Radiative cooling dynamics of isolated N_2O^+ ions in a cryogenic electrostatic ion storage ring, *Phys. Rev. A* **102**, 023119 (2020).
- [97] A. P. O'Connor, A. Becker, K. Blaum, C. Breitenfeldt, S. George, J. Göck, M. Grieser, F. Grussie, E. A. Guerin, R. von Hahn, *et al.*, Photodissociation of an internally cold beam of CH^+ ions in a cryogenic storage ring, *Phys. Rev. Lett.* **116**, 113002 (2016).
- [98] Á. Kálosi, M. Grieser, R. von Hahn, U. Hechtfisher, C. Krantz, H. Kreckel, D. Müll, D. Paul, D. W. Savin, P. Wilhelm, A. Wolf, and O. Novotný, Laser probing of the rotational cooling of molecular ions by electron collisions, *Phys. Rev. Lett.* **128**, 183402 (2022).
- [99] L. H. Andersen, A. P. Rasmussen, H. B. Pedersen, and N. Klinkby, Time-resolved cryogenic action spectroscopy of dipole-bound states in phenoxide, *Phys. Rev. Lett.* **134**, 193002 (2025).
- [100] H. Kreckel, 2026, “ H_3^+ Spectroscopy in the Cryogenic Storage Ring”, Edmond, V1, 2026, <https://doi.org/10.17617/3.LPUACU>.